AD-A045 862

CASE WESTERN RESERVE UNIV CLEVELAND OHIO HIGH ENERGY NITROGEN COMPOUNDS. (U) JUL 77 G A OLAH

F/G 19/1

UNCLASSIFIED

ARO-12915.3-C

DAHC04-75-G-0110 NL

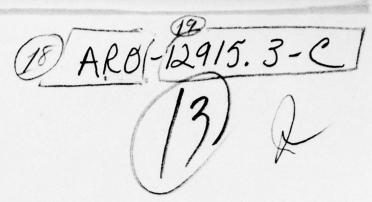
| OF | ADA045862











HIGH ENERGY NITROGEN COMPOUNDS.

PINAL REPORT. 1 Apr 75-14 Jul 73

GEORGE A. CLAH
PHINCIPAL INVESTIGATOR

April 1, 1975 - July 14, 1977

U.S. ARMY RESEARCH OFFICE

DDC

DAHCO 4-75-G-011b

ARO PROPOSAL NUMBER: 12915C

CASE WESTERN RESERVE UNIVERSITY

CASE WESTERN RESERVE UNIVERSIT

44106

DOC FILE COPY

DISTRIBUTION STATEMENT A

Approved for public released Distribution Unlimited

402 490

nt

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
HIGH ENERGY NITROGEN COMPOUNDS	FINAL 4-1-75-7-14-97
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(*)
GEORGE A. OLAH	DA1C04-75-G-0110 mm
PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
CASE WESTERN RESERVE UNIVERSITY	
DEPT. OF CHEMISTRY CLEVELAND, ONIO 11106	
1. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
U. S. Army Research Office .	14-1-75 - 7-14-77 13. NUMBER OF PAGES
Post Office Box 12211	13. NUMBER OF PAGES
Research Triangle Park, NC 27709	4
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)	15. SECURITY CLASS. (of this report)
	Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA
16. DISTRIBUTION STATEMENT (of this Report)	L AA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, If different from Report)

NA

## 18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Nitration, TNT, TNB, Polynitrates, N-nitro compounds

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The objective of the work was to extend our basic knowledge of nitration, the fundamental reaction producing high energy nitrogen compounds. Studies included exploration of new areas of aliphatic electrophilic nitration, improved preparative routes to known high energy compounds such as TNT and TNB (1.3.5-trinitrobenzene) and safe new methods to prepare 0- and nitrogen compounds.

DD 1 JAN 73 1473

EDITION OF I NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

## FINAL REPORT GRANT NO. DAHCO4-75-6-0110

## HIGH ENERGY NITROGEN COMPOUNDS

The objective of the work was to extend our basic knowledge of nitration, the fundamental reaction producing high energy nitrogen compounds. Studies included exploration of new areas of aliphatic electrophilic nitration, improved preparative routes to known high energy compounds such as TNT and TNB (1,3,5-trinitrobenzene) and safe new methods to prepare 0- and nitrogen compounds.

All objectives of the research project were met. A new, efficient method for the trinitration of benzene to trinitrobenzene (TNB) was worked out using nitric-fluorosulfuric acid.

Mechanistic studies of the nitration of aromatics (both electrophilic, nucleophilic and free radical) were continued. The independence of substrate from regioselectivity in the nitration of reactive aromatics (toluene, anisole, o-xylene) was firmly established, clearly indicating the involvement of two separate reaction steps. No simple, linear relationship can thus exist. Free radical nitration and nitrolysis of aromatics, such as diarylhalonium ions, was also studied.

The use of pyridinium polyhydrogen fluoride as reaction medium for nitronium salt nitrations was found to be highly effective. This solvent has no oxidizing ability, is an excellent solvent for both organic substrates and nitronium salts alike, and thus shows promise in minimizing oxidative side reactions.

The nitration of aliphatic and cycloaliphatic hyd ons was continued under electrophilic conditions. Further preparative for nitroaliphatic compounds, including nitroalkanes, nitroalkanes and nitroalimentane were developed. Work continued on the possible synthesis of tetranitroadamantane and hexanitrobenzene.

The following list of publications refers to published papers containing details of the work.

ACCESSION for NTIS	White Section
DDC UNANNOUNCED	Buff Section
	AVAILABILITY CODES
$\alpha$	

G. A. Olah, A. Germain, H. C. Lin and D. A. Forsyth

Bonds. XVIII. Indication of Protosolvated de facto Substituting Agents in the Reactions of Alkanes with Acetylium and Nitronium Ions in Superacidic Media. J. Am. Chem. Soc. <u>97</u>, 2928 (1975).

Electrophilic Reactions at Single

G. A. Olah

Electrophilic Nitration (invited paper presented at the Symposium on Industrial and Laboratory Nitration of the American Chemical Society, Philadelphia Meeting, April 1975).

ACS Symposium Monograph Series, Vol. 22, eds. L. F. Albright and C. Hanson, pp. 1-47 (1976).

G. A. Olah, H. C. Lin and A. Serianz

Synthetic Methods & Reactions. XVI. The Nitramine Rearrangement of N-Nitrodimethylanilines. A Novel Route for the Conversion of 3-Nitro-o-xylene. Synthesis 42 (1976).

G. A. Olah, H. C. Lin, J. A. Olah and S. C. Narang

Variation in the Isomer Distribution in the Electrophilic Nitration of Toluene, Anisole and ortho-Xylene. The Independence of High Regioselectivity from the Reactivity of the Reagent. Proc. Natl. Acad. Sci. (in press).

G. A. Olah, T. Sakakibara and G. Asensio

Improved Preparation, Carbon-13 NMR Spectroscopic Structural Study and Nucleophilic Nitrolysis of Diarylhalonium Ions. J. Org. Chem (in press).